

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



10/538682

(43) International Publication Date
15 July 2004 (15.07.2004)

PCT

(10) International Publication Number
WO 2004/058857 A2

(51) International Patent Classification⁷: C08G 77/04

(21) International Application Number:
PCT/US2003/040277

(22) International Filing Date:
17 December 2003 (17.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/435,824 20 December 2002 (20.12.2002) US

(71) Applicant (for all designated States except US): DOW CORNING CORPORATION [US/US]; 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHAPMAN, Brian, Douglas [US/US]; 401 Lingle Lane, Midland, MI 48640 (US). DURFEE, Loren, Dean [US/US]; 1807 Burlington Drive, Midland, MI 48642 (US). MITCHELL, Timothy, Paul [US/US]; 508 Clarion Street, Clio, MI 48420 (US). VAN DORT, Paul, Cornelius [US/US]; 3051 North Lakeview Drive, Sanford, MI 48657 (US). TONGE, James [US/US]; 3105 North Lakeview Drive, Sanford, MI 48657 (US).

(74) Common Representative: SCADUTO, Patricia, M.; IP Department - MS CO 1232, Dow Corning Corporation, 2200 West Salzburg Road, P.O. Box 994, Midland, MI 48686-0994 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BRANCHED POLYMERS FROM ORGANOHYDROGENSILICON COMPOUNDS

(57) Abstract: A method comprising heating in the presence of a catalyst, a mixture comprising (i) a reaction product obtained by mixing in the presence of a platinum group metal-containing catalyst at least one organohydrogensilicon compound containing at least one silicon-bonded hydrogen atom per molecule and at least one compound having at least one aliphatic unsaturation; (ii) at least one endblocker, and optionally (iii) at least one organosiloxane chosen from a hydrolyzate or a cyclosiloxane, so to cause polymerization of components (i), (ii), and optionally (iii) to form branched polymers.

WO 2004/058857 A2

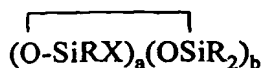
BRANCHED POLYMERS FROM ORGANOHYDROGENSILICON COMPOUNDS**DESCRIPTION**

[0001] This invention relates to a method comprising heating in the presence of a catalyst, a mixture comprising (i) a reaction product obtained by mixing in the presence of a platinum group metal-containing catalyst at least one organohydrogensilicon compound containing at least one silicon-bonded hydrogen atom per molecule and at least one compound having at least one aliphatic unsaturation; (ii) at least one endblocker, and optionally (iii) at least one organosiloxane chosen from a hydrolyzate or a cyclosiloxane, so to cause polymerization of components (i), (ii), and optionally (iii) to form branched polymers.

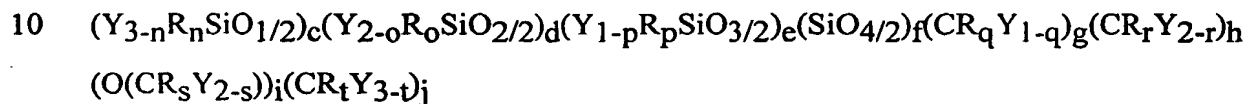
[0002] Polymers containing branching and methods for making them are known. However, due to the starting materials generally used, it is difficult to independently control the many parameters of polymer architecture oftentimes resulting in polymer species having undesired end-group functionality. In addition, methodologies reported in the literature for synthesis of branched polymers using components containing silicon-alkylene linkages result in products which exhibit low viscosity, low Dp (degree of polymerization), low branching content or high viscosity, high Dp, high branching content. One object of the present invention is to use a cyclic branched intermediate without end-groups so to independently control properties such as branching, end-group level, end-group identity, and Dp. Another object is to produce low viscosity, high Dp, highly branched polymers.

[0003] The present invention is a method of preparing branched polymers comprising heating in the presence of a catalyst, a mixture comprising

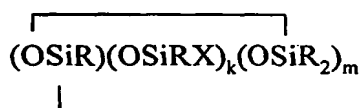
(i) a reaction product obtained by mixing in the presence of a platinum group metal-containing catalyst at least one organohydrogensilicon compound containing at least one silicon-bonded hydrogen atom per molecule and at least one compound having at least one aliphatic unsaturation; where the organohydrogensilicon compound is described by formula (I)



where each R is independently selected from a hydrogen atom and a monovalent hydrocarbon group comprising 1 to 20 carbon atoms which is free from aliphatic unsaturation, a is an integer from 1 to 18, b is an integer from 1 to 19, a + b is an integer from 3 to 20, each X is an independently selected functional group selected from a halogen atom, an ether group, an alkoxy group, an alkoxyether group, an acyl group, or a silyl group, or a $-Z-R^4$ group, where each Z is independently selected from an oxygen and a divalent hydrocarbon group comprising 2 to 20 carbon atoms, each R^4 group is independently selected from $-BR_uY_{2-u}$, $-SiR_vY_{3-v}$, or a group described by formula (II):



where B refers to boron, each R is as described above, the sum of c+d+e+f+g+h+i+j is at least 2, n is an integer from 0 to 3, o is an integer from 0 to 2, p is an integer from 0 to 1, q is an integer from 0 to 1, r is an integer from 0 to 2, s is an integer from 0 to 2, t is an integer from 0 to 3, u is an integer from 0 to 2, v is an integer from 0 to 3, each Y is an independently selected functional group selected from a halogen atom, an ether group, an alkoxy group, an alkoxyether group, an acyl group, or a silyl group, or a Z-G group, where Z is as described above, each G is a cyclosiloxane described by formula (III):



where R and X are as described above, k is an integer from 0 to 18, m is an integer from 0 to 18, k+m is an integer from 2 to 20, provided in formula (II) that one of the Y groups is replaced by the Z group bonding the R^4 group to the cyclosiloxane of formula (I), and provided further at least one X group of Formula (I) is a $-Z-R^4$ group;

(ii) at least one endblocker described by formula (IV) $R'_3SiO(MeR'SiO)_zSiR'_3$, where z ranges from 0 to 150 and each R' is independently chosen from alkyl, aryl, alkenyl, dienyl or functional alkyls where the functionality may be fluoro, fluoroether, polyether, ether, aryl, silyl, siloxy, carboxy, glycosidyl or acrylate, and optionally

(iii) at least one organosiloxane chosen from a hydrolyzate described by formula (V) $\text{HO}(\text{MeR}'\text{SiO})_{y'}\text{H}$ and a cyclosiloxane described by formula (VI) $(\text{MeR}'\text{SiO})_y$ where y is an integer from 3 to 30, y' is an integer from 1 to 500, and each R' is as described above; so to cause polymerization of components (i), (ii), and optionally (iii) to form branched polymers.

5

[0004] Component (i) of the present method comprises a reaction product obtained by mixing in the presence of a platinum group metal-containing catalyst at least one organohydrogensilicon compound containing at least one silicon-bonded hydrogen atom per molecule as described by formula (I) above and at least one compound having at least one aliphatic unsaturation.

10

[0005] With respect to the organohydrogensilicon compounds used to make component (i) for the present method, each R group described in formulas (I), (II), and (III) is independently selected from a hydrogen atom and a monovalent hydrocarbon group comprising 1 to 20 carbon atoms free from aliphatic unsaturation. Each monovalent hydrocarbon group of R can be linear, branched or cyclic. Each monovalent hydrocarbon group of R can be unsubstituted or substituted with halogen atoms. The monovalent hydrocarbon group of R can be exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, hexyl, octyl, 3,3,3-trifluoropropyl, nonafluorobutylethyl, chloromethyl, and decyl, cycloaliphatic groups such as cyclohexyl, aryl groups such as phenyl, tolyl, and xylyl, chorophenyl, and aralkyl groups such as benzyl, styryl and alpha-methylstyryl. It is preferred that each R group is independently selected from hydrogen atoms, alkyl groups comprising 1 to 8 carbon atoms, or aryl groups comprising 6 to 9 carbon atoms. It is most preferred that each R group is independently selected from hydrogen, methyl, alpha-methylstyryl, 3,3,3-trifluoropropyl and nonafluorobutylethyl. Each R can be identical or different, as desired.

15

20

25

[0006] In formula (I), a is an integer from 1 to 18, b is an integer from 1 to 19, preferably from 2 to 19, and $a + b$ is an integer from 3 to 20.

[0007] In formulas (I) and (III) of the organohydrogensilicon compound, each X is an independently selected functional group selected from a halogen atom, an ether group, an alkoxy group, an alkoxyether group, an acyl group, or a silyl group, or a $-\text{Z}-\text{R}^4$ group.

30

[0008] The functional groups represented by X are selected from halogen atoms, ether groups, alkoxy groups, alkoxyether groups, acyl groups, or silyl groups. Examples of useful halo groups include chloro, fluoro, and bromo. Examples of useful alkoxy groups include methoxy, ethoxy, and isopropoxy. Examples of useful alkoxyether groups include ethylene glycol monopropyl ether and ethylene glycol monoethyl ether. Other useful functional groups are derived by hydrosilylation of the vinyl group from methylvinylether, methylvinylketone, vinylacetate, vinylbenzoate, vinylacrylate, vinylstearate, vinyldecanoate, vinylmethacrylate, trimethylvinylsilane, triethylvinylsilane, vinyltrimethoxysilane, vinyltriacetoxysilane, phenylvinylether, phenylvinylketone, and allyl aldehyde with an Si-H from the siloxane precursor to formulas (I) or (III).

[0009] When X is a functional group, it is preferred that each X is independently selected from chloro, methoxy, or isopropoxy. Each X of formulas (I) and (III) may also comprise a -Z-R⁴ group. It is more preferred that X is a -Z-R⁴ group.

[0010] Each Z is independently selected from oxygen and divalent hydrocarbon groups comprising 2 to 20 carbon atoms. Examples of the divalent hydrocarbon group comprising 2 to 20 carbon atoms represented by Z include alkylene radicals such as methylene, ethylene, methylmethylene, propylene, isopropylene, butylene, pentylene, hexylene, and octadecylene; alkenylene radicals such as vinylene, allylene, butenylene, and hexenylene; arylene radicals such as phenylene and xylylene; aralkylene radicals as benzylene; and alkarylene radicals such as tolylene. Preferably, Z is a divalent hydrocarbon group comprising 2 to 18 carbon atoms. It is more preferred for Z to be an alkylene group, with an alkylene group comprising 2 to 8 carbon atoms being most preferred.

[0011] Each R⁴ group is selected from -BR_uY_{2-u}, -SiR_vY_{3-v}, or a group described by formula (II): (Y_{3-n}R_nSiO_{1/2})_c(Y_{2-o}R_oSiO_{2/2})_d(Y_{1-p}R_pSiO_{3/2})_e(SiO_{4/2})_f(CR_qY_{1-q})_g(CR_rY_{2-r})_h(O(CR_sY_{2-s}))_i(CR_tY_{3-t})_j, where R, Y, c, d, e, f, g, h, i, j, n, o, p, q, r, s, t, u, v are as described above, provided in formula (II) that one of the Y groups is replaced by the Z group bonding the R⁴ group to the cyclosiloxane of formula (I).

[0012] In formula (II) of the organohydrogensilicon compound, the sum of $c+d+e+f+g+h+i+j$ is at least 2, preferably from 2 to 5300, more preferably from 2 to 1000. Preferably, subscript c is an integer from 0 to 50, with 2 to 15 being more preferred, and 2 to 10 being most preferred. Preferably, subscript d is an integer from 0 to 5000, with 0 to 1000 being more preferred, and 1 to 50 being most preferred. Preferably, subscript e is an integer from 0 to 48, with 0 to 13 being more preferred, and 0 to 8 being most preferred. Preferably, subscript f is an integer from 0 to 24, with 0 to 6 being more preferred, and 0 to 4 being most preferred. Preferably, subscript g is an integer from 0 to 50, with 0 to 20 being more preferred, and 0 to 10 being most preferred. Preferably, subscript h is an integer from 0 to 50, with 0 to 20 being more preferred, and 0 to 10 being most preferred. Preferably, subscript i is an integer from 0 to 50, with 0 to 20 being more preferred, and 0 to 10 being most preferred. Preferably, subscript j is an integer from 0 to 50, with 0 to 15 being more preferred, and 0 to 10 being most preferred.

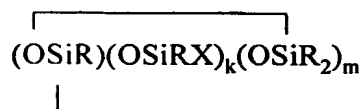
[0013] In formula (II) of the organohydrogensilicon compound, n is an integer from 0 to 3, preferably from 2 to 3; o is an integer from 0 to 2, preferably from 1 to 2; p is an integer from 0 to 1, preferably 1; q is an integer from 0 to 1, preferably 1; r is an integer from 0 to 2, preferably from 1 to 2; s is an integer from 0 to 2, preferably from 1 to 2; and t is an integer from 0 to 3, preferably from 2 to 3. Notwithstanding the above, since the R^4 group as described by formula (II) is connected to the cyclosiloxane described by formula (I) via a Z group, one of the Y groups present in the R^4 group described by formula (II) will be replaced by a Z group.

[0014] In addition to a group described by formula (II), each R^4 group is independently selected from $-BR_uY_{2-u}$, and $-SiR_vY_{3-v}$ where B refers to boron, u is an integer from 0 to 2, preferably from 1 to 2 and v is an integer from 0 to 3, preferably from 2 to 3. Examples of these R^4 groups are derived from borane or silanes, such as for example, trivinylborane, diallyldimethylsilane, divinyltrimethylsilane and vinyltrimethylsilane.

[0015] Each Y of R^4 is an independently selected functional group selected from a halogen atom, an ether group, an alkoxy group, an alkoxyether group, an acyl group, or a silyl group,

or a -Z-G group. The functional groups are exemplified as described above for X. The Z group is also as described above.

Each G is a cyclosiloxane described by formula (III):



where R and X are as described above, k is an integer from 0 to 18, m is an integer from 0 to 18, and k+m is an integer from 2 to 20.

10 **[0016]** In formula (III) of the organohydrogensilicon compound, each k is an integer from 0 to 18, preferably from 1 to 3.

[0017] In formula (III) of the organohydrogensilicon compound, each m is an integer from 0 to 18, preferably from 1 to 10, most preferably from 2 to 4.

15 **[0018]** The sum of k+m is an integer from 2 to 20, preferably from 2 to 6, most preferably from 2 to 5.

[0019] The Y group of formula (II) is preferably a -Z-G group. Although it is not required
20 for there to be any -Z-G groups in the organohydrogensilicon compounds useful in the present method, it is preferred that on average the organohydrogensilicon molecules contain at least 1 -Z-G group with at least 2 -Z-G groups being more preferred.

[0020] The R⁴ group described by formula (II) can be linear, cyclic, branched or resinous.
25 The R⁴ group described by formula (II) can be a siloxane material where the polymer chain units contain only siloxane units, or it can be a mixture of siloxane units with hydrocarbon units or oxyhydrocarbon units, where oxyhydrocarbon refers to a hydrocarbon group which also includes at least one oxygen atom, or it can be a hydrocarbon material where the polymer chain units contain only hydrocarbon units or oxyhydrocarbon units. It is preferred

that the R^4 group comprises hydrocarbon units, oxyhydrocarbon units, or siloxane units, with siloxane units being more preferred.

[0021] Examples of preferred R^4 groups described by formula (II) include $-CH_2CH_2-$,

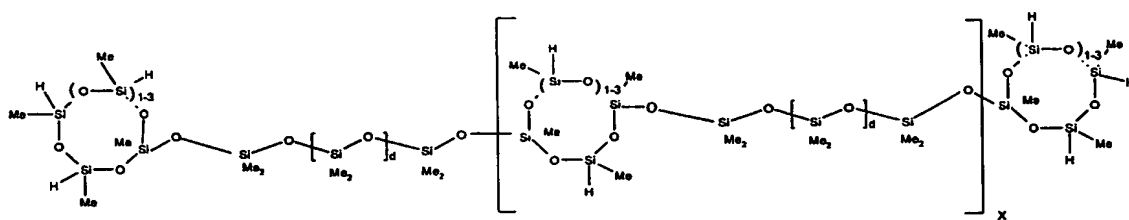
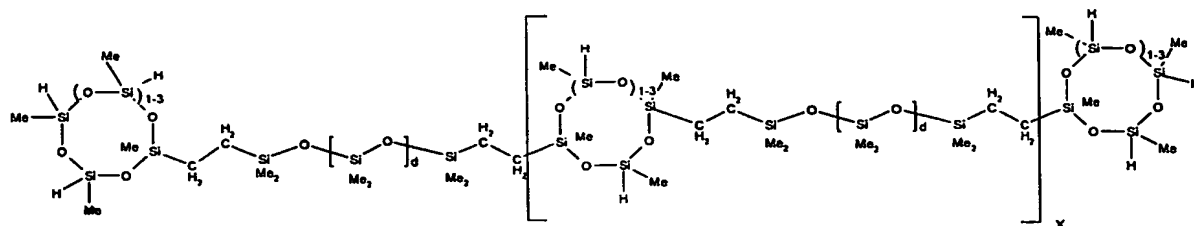
5 $-CH_2CH_2CH_2CH_2-$, $-O(CH_2CH_2O)_{z'}-$, where $z' = 1-100$, $-O(CH_2CH_2CH_2O)_{z''}-$, where $z'' = 1-100$ and siloxane groups described by $-R_2SiO(R_2SiO)_dSiR_2-Z-G$, $-R_2SiOSiR_3-$, $R_2SiOSiR_2-Y$, $-RSi(OSiR_3)_2$, where d is an integer from 1 to 50 and Z , G , and R are as described above. More preferred R^4 groups are the siloxane groups as described above when R is methyl, and d is an average of 8.

10 [0022] With respect to the organohydrogensilicon compounds useful in the present method, it is preferred that at least one X group of Formula (I) is a $-Z-R^4$ group.

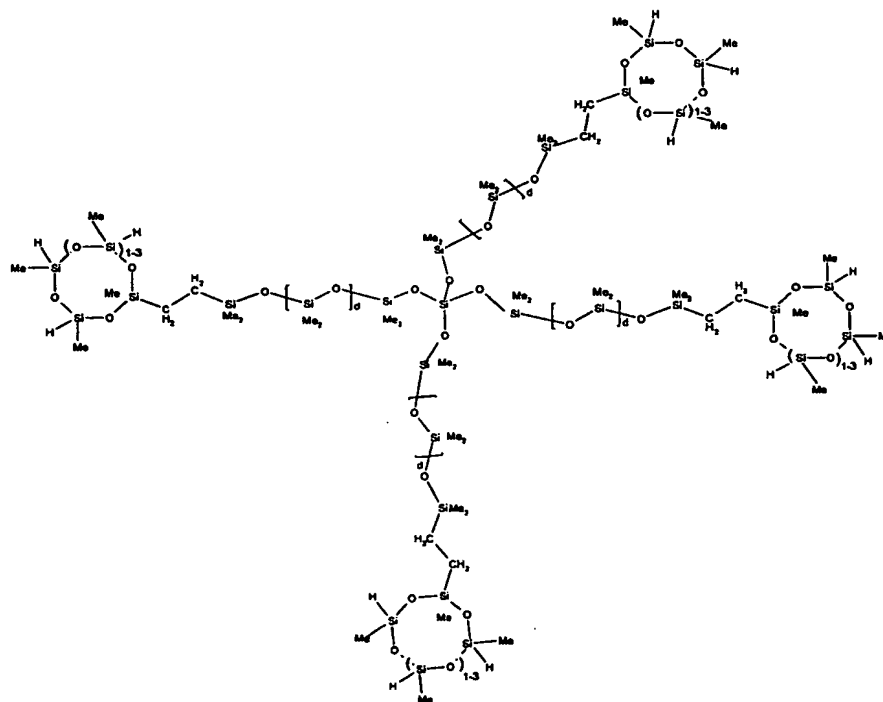
[0023] It is also preferred that the organohydrogensilicon compounds have a viscosity from
15 5 to 50,000 mPa.s, more preferred from 10 to 10,000 mPa.s and most preferred from 25 to 2,000 mPa.s.

[0024] The organohydrogensilicon compounds useful for making component (i) of the present method contain at least one silicon-bonded hydrogen atom per molecule. Preferably,
20 the organohydrogensilicon compounds contain at least 2 silicon-bonded hydrogen atoms per molecule. It is most preferred that the organohydrogensilicon compounds contain at least 3 silicon-bonded hydrogen atoms per molecule.

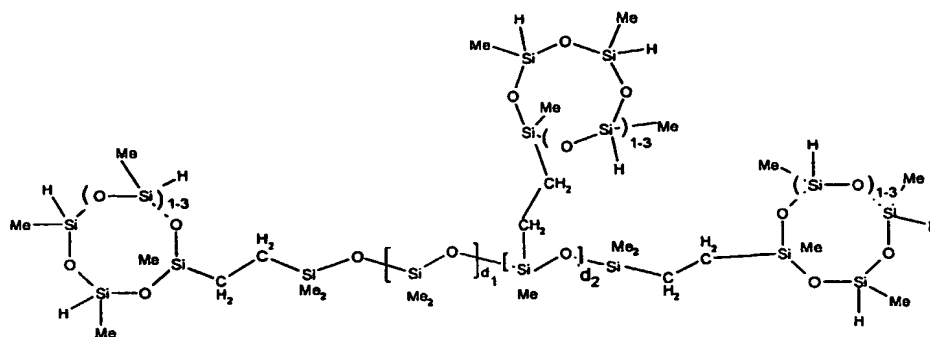
[0025] Examples of the types of organohydrogensilicon compounds included in the scope
25 of the present invention are as follows where Me is methyl, d (which equals $d_1 + d_2$) is as described above, and x can range from 1 to 100; preferably 1 to 20.



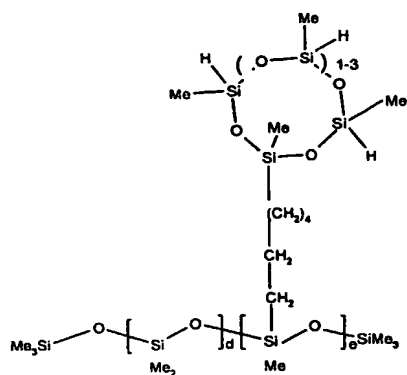
5



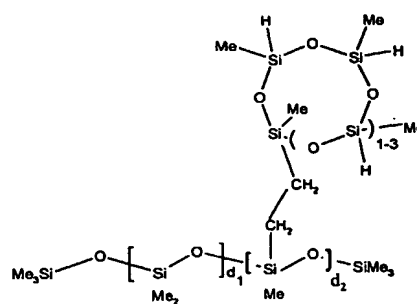
5



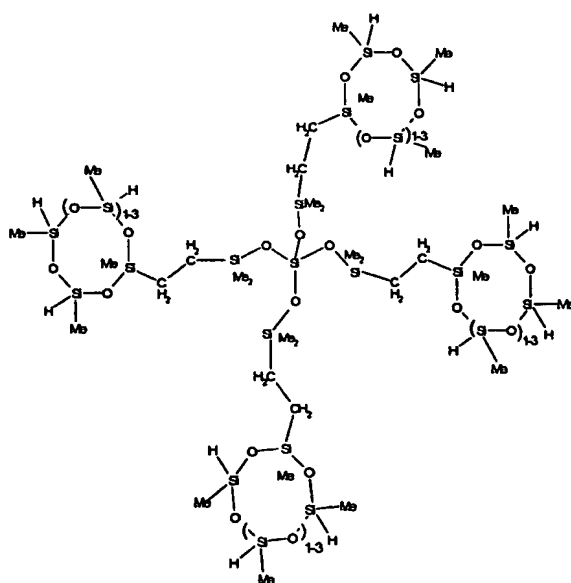
10

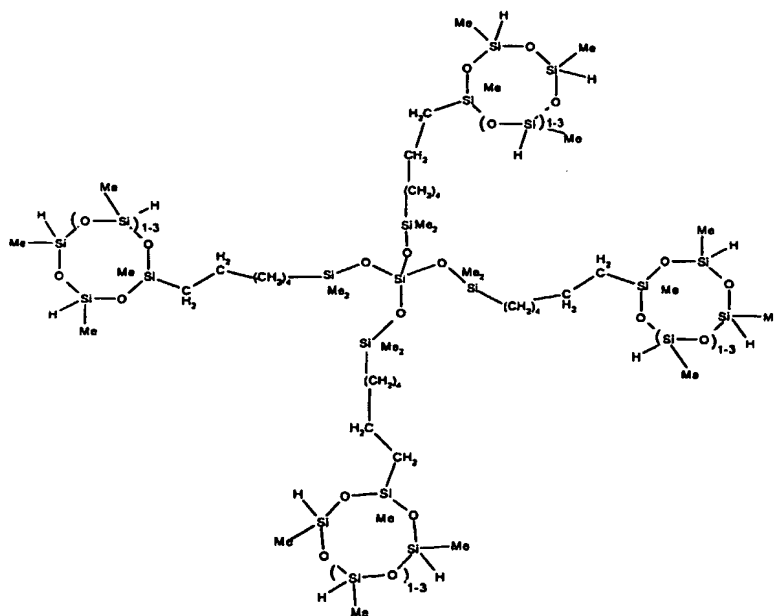
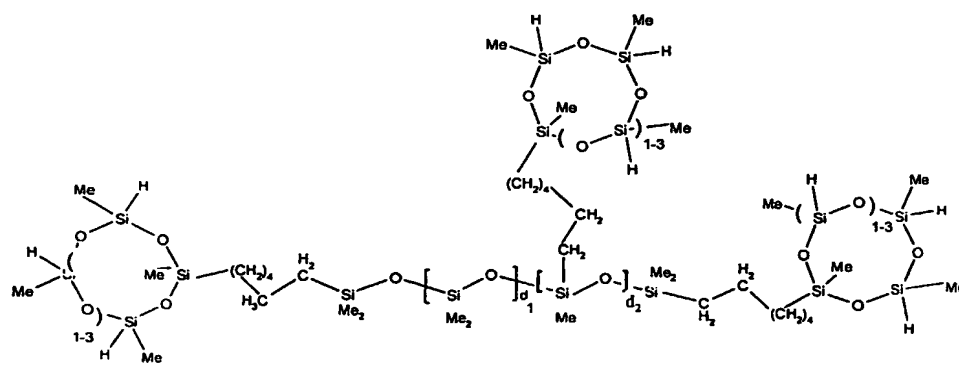
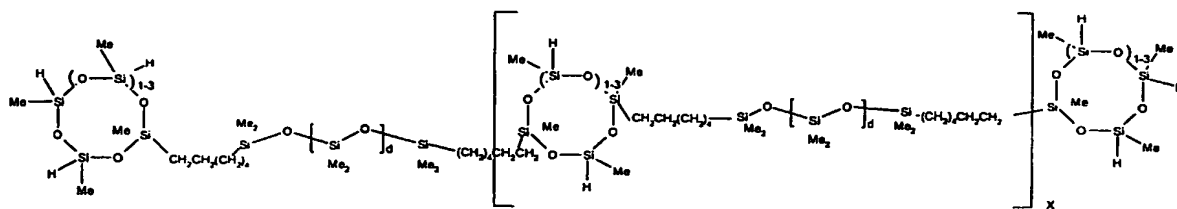


15

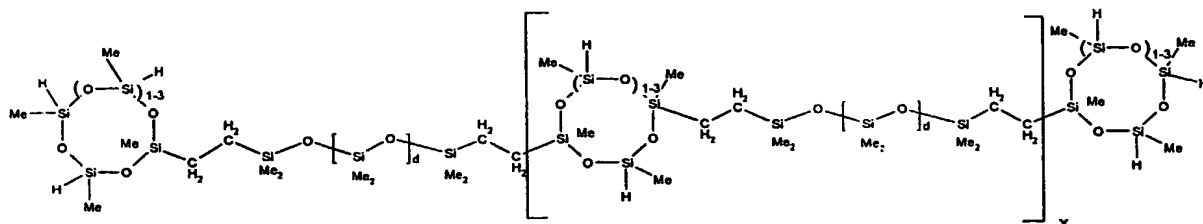


20





[0026] The most preferred organohydrogensilicon compounds described by formula (I) are as follows where Me is methyl, d is an average of 8, and x is an integer from 0 to 15:



5

[0027] The organohydrogensilicon compounds can be made in a straightforward manner, for example via a platinum catalyzed coupling of (A) organohydrogen cyclosiloxanes having at least 2 Si-H groups per molecule with (B) a reactant containing at least one aliphatic unsaturation, hydroxy functionality or a mixture of both at temperatures from 20 to 150 °C.

10 Generally, the ratio of Si-H to aliphatic unsaturation or Si-H to hydroxy functionality useful to prepare the organohydrogensilicon compounds useful in the present method is at least 2.5:1.

[0028] Various organohydrogensilicon compounds and methods of making the
 15 organohydrogensilicon compounds are also described in U.S. Pat Appln. No. 60/377,425 and PCT Appln. No. US03/13203 which are hereby incorporated by reference. The desired product is a function not only of the reactants but also of the reaction stoichiometry. The reaction can be conducted by premixing the reactants followed by catalysis or by using one of the reactants as a controlling reagent. Since it is desired to react aliphatically unsaturated
 20 groups or hydroxy groups randomly with as many Si-H containing molecules as possible, the reaction may be conducted by premixing component (A) and (B) as described above, and then catalyzing the premix; by pre-catalyzing component (A) followed by controlled introduction of component (B), by precatalyzing component (B) and then adding this premix to component (A), or by something in between these three extremes.

25

[0029] The organohydrogensilicon compounds may be a single species or a mixture of different species.

[0030] The compounds having at least one aliphatic unsaturation used to make component (i) can be linear, branched, resinous or cyclic and can be monomers or polymers (including copolymers, terpolymers etc.) provided there is at least one aliphatic unsaturation. The compounds containing aliphatic unsaturation have alkenyl (also described as olefinic) unsaturation or alkynyl (also described as acetylenic) unsaturation. These compounds are well-known in the art of hydrosilylation and are disclosed in such patents as U.S. Pat. No. 3,159,662 (Ashby), U.S. Pat. No. 3,220,972 (Lamoreaux)), and U.S. Pat. No. 3,410,886 (Joy), which disclosures of said compounds are incorporated herein by reference. In instances where these unsaturated compounds contain elements other than carbon and hydrogen, it is preferred that these elements be oxygen, nitrogen, silicon, a halogen, or a combination thereof.

[0031] The aliphatically unsaturated compound can contain one or more carbon-carbon multiple bonds. Representative examples of the aliphatically unsaturated hydrocarbons which can be employed include mono-olefins, for example, ethene (ethylene), propene, 1-pentene and 1-hexene, diolefins, for example, divinylbenzene, butadiene, 1,5-hexadiene and 1-buten-3-yne, cycloolefins, for example, cyclohexene and cycloheptene, and monoalkynes, for example, acetylene, propyne and 1-hexyne.

[0032] Oxygen-containing aliphatically unsaturated compounds can also be used, especially where the unsaturation is ethylenic, such methylvinyl ether, divinylether, phenylvinyl ether, monoallyl ether of ethylene glycol, allyl aldehyde, methylvinyl ketone, phenylvinyl ketone, acrylic acid, methacrylic acid, methyl acrylate, allyl acrylate, methyl methacrylate, allyl methacrylate, vinylacetic acid, vinyl acetate, and linolenic acid.

[0033] Heterocyclic compounds containing aliphatic unsaturation in the ring, such as dihydrofuran, and dihydropyran, are also suitable to react with the organohydrogensilicon compounds.

[0034] Halogenated derivatives of the previously mentioned aliphatically unsaturated compounds can be employed, including acyl chlorides as well as compounds containing a halogen substituent on a carbon atom other than a carbonyl carbon atom. Such halogen-containing compounds include, for example, vinyl chloride, and the vinylchlorophenyl esters.

5

[0035] Unsaturated compounds containing nitrogen substituents such as acrylonitrile, N-vinylpyrrolidone, alkyl cyanide, and nitroethylene, are also useful.

[0036] Other compounds useful for making component (i) include polymers (including copolymers, terpolymers etc.) of the various compounds described above provided there is at least one aliphatic unsaturation. Examples include polymers derived from oxyhydrocarbon repeating units such as poly(alkyleneglycol) polymers with one or two allyloxy or vinyloxy end-cap groups. Common examples are polymers and copolymers of ethylene glycol and/or propylene glycol.

15

[0037] Another useful type of compound which can be reacted with the organohydrogensilicon compounds is that containing silicon, such as those compounds commonly referred to as organosilicon compounds. The useful organosilicon compounds have at least one aliphatically unsaturated group attached to silicon per molecule. The aliphatically unsaturated organosilicon compounds include silanes, siloxanes, silazanes, as well as monomeric or polymeric materials containing silicon atoms joined together by hydrocarbyl groups such as alkylene or polyalkylene groups or arylene groups. The silicon-modified organic compounds useful in making component(i) include organic monomers or polymers such as described above having at least one silicon atom attached as a silane or a siloxane segment. The silicon-containing units can contain aliphatic unsaturation and can be attached at the terminal and/or pendant positions on the organic polymer chain or as a copolymer.

20

25

[0038] Silanes useful in the present invention can be described by formula (VII)

30



where each R^1 is an independently selected monovalent hydrocarbon radical comprising 1 to 20 carbon atoms free from aliphatic unsaturation, each Q is independently selected from a monovalent hydrocarbon group comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation, a monovalent oxyhydrocarbon group comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation, a halogen atom, an alkoxy group, or an acyl group, provided at least one Q group has at least one aliphatic unsaturation, and w is an integer from 0 to 3.

[0039] In formula (VII), each R^1 group is an independently selected monovalent hydrocarbon group comprising 1 to 20 carbon atoms which are free from aliphatic unsaturation. Each R^1 group can be linear, branched or cyclic. R^1 can be unsubstituted or substituted with halogen atoms. The monovalent hydrocarbon group of R^1 can be exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, hexyl, octyl, 3,3,3-trifluoropropyl, chloromethyl, and decyl, cycloaliphatic groups such as cyclohexyl, aryl groups such as phenyl, tolyl, and xylyl, chorophenyl, and aralkyl groups such as benzyl, styryl and alpha-methylstyryl. It is preferred that each R^1 group is an independently selected alkyl group comprising 1 to 8 carbon atoms or aryl group comprising 6 to 9 carbon atoms. It is most preferred that each R^1 group is independently selected from methyl, alpha-methylstyryl, 3,3,3-trifluoropropyl and nonafluorobutylethyl. Each R^1 can be identical or different, as desired.

[0040] In formula (VII), each Q is independently selected from a monovalent hydrocarbon group comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation, a monovalent oxyhydrocarbon group comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation, a halogen atom, an alkoxy group, or an acyl group, provided at least one Q group has at least one aliphatic unsaturation.

[0041] The aliphatic unsaturations of Q can be found in a pendant position to the hydrocarbon chain, at the end of the hydrocarbon chain, or both, with the terminal position being preferred. Each monovalent hydrocarbon and oxyhydrocarbon group can be linear, branched, or cyclic.

[0042] Examples of monovalent hydrocarbon groups comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation of Q include alkenyl groups such as vinyl, allyl, 3-butenyl, 4-pentenyl, 5-hexenyl, cyclohexenyl, 6-heptenyl, 7-octenyl, 8-nonenyl, 9-decenyl, 10-undecenyl, and diene groups comprising 4 to 20 carbon atoms such as 4,7-octadienyl, 5,8-nonadienyl, 5,9-decadienyl, 6,11-dodecadienyl, 4,8-nonadienyl, and 7,13-tetradecadienyl.

[0043] Examples of monovalent oxyhydrocarbon groups comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation of Q include alkenyloxy groups such as oxybutylvinylether and alkynyloxy groups such as propargyloxy or hexynyloxy.

[0044] Examples of halogen atoms of Q include chloro, fluoro, and bromo atoms. Examples of alkoxy groups of Q include methoxy, ethoxy, and isopropoxy. An example of an acyl group of Q is acetoxy.

[0045] Preferably, each Q is an independently selected monovalent hydrocarbon group comprising 2 to 20 carbon atoms having at least one aliphatic unsaturation. More preferably, each Q is an independently selected alkenyl group comprising 2 to 20 carbon atoms, with an alkenyl group comprising 2 to 8 carbon atoms being most preferred for Q.

[0046] Examples of silanes include vinyltrimethylsilane, vinyldimethylchlorosilane, vinylmethylchlorosilane, hexenyldimethylchlorosilane, and hexenylmethylchlorosilane, and vinyltriacetoxysilane.

[0047] Examples of silane-modified organic polymers are silylated polymers derived from olefins, isomonoolefin, dienes, ethylene or propylene oxides, and vinyl aromatic monomers having 2 to 20 carbon atoms such as the silane-grafted copolymers of isomonoolefin and vinyl aromatic monomer as discussed in U.S. Patent Nos. 6,177, 519 and 5,426,167. Other representative silicon-modified organic polymers are illustrated by, but not limited to alkenylsiloxo-functional polymers such as vinylsiloxo-, allylsiloxo-, and hexenylsiloxo-organic polymers and siloxane-organic block copolymers.

[0048] Examples of organosilicon polymers and silicon-modified organic polymers include trimethylsiloxy-terminated polydimethylsiloxane-polymethylvinylsiloxane copolymers, trimethylsiloxy-terminated polydimethylsiloxane-polymethylhexenylsiloxane copolymers, trimethylsiloxy-terminated polymethylvinylsiloxane polymers, trimethylsiloxy-terminated polymethylhexenylsiloxane polymers, polydimethylsiloxane polymers with one or two vinyl or hexenyl terminations, poly(dimethylsiloxane-monomethylsilsesquioxane) polymers with one or multiple vinyl or hexenyl terminations, trimethylsiloxy terminated poly(dimethylsiloxane-vinylmethylsiloxane-methylsilsesquioxane) polymers, trimethylsiloxy terminated poly(dimethylsiloxane-hexenylmethylsiloxane-methylsilsesquioxane) polymers, poly(dimethylsiloxane-silicate) copolymers with one or multiple vinyl or hexenyl terminations, trimethylsiloxy terminated poly(dimethylsiloxane-vinylmethylsiloxane-silicate) copolymers and trimethylsiloxy terminated poly(dimethylsiloxane-hexenylmethylsiloxane-silicate) copolymers, poly(dimethylsiloxane-hydrocarbyl) copolymers with one or two vinyl or hexenyl terminations, poly(dimethylsiloxane-polyoxyalkylene) block copolymers with one or two vinyl or hexenyl termination, polyisobutylene and polydimethylsiloxane-polyisobutylene block copolymers with one or two alkenyl terminations.

[0049] At least one compound having at least one aliphatic unsaturation is reacted with the organohydrogensilicon compounds described above to form component (i) in the present method. Therefore, one compound having at least one aliphatic saturation or a mixture of different compounds may be used. In addition, the compound can also have one or more aliphatic unsaturations. In preferred embodiments, the compound comprises at least one compound having at least one aliphatic unsaturation. Most preferred is when only a single type of compound having one aliphatic unsaturation is used.

[0050] The compounds comprising at least one aliphatic unsaturation may be a single species or a mixture of different species. They are commercially available or may be made by methods known in the art.

[0051] The platinum group metal-containing catalyst useful for catalyzing the hydrosilylation reaction between the organohydrogensilicon compound and the compound having at least one aliphatic unsaturation comprises any catalyst typically employed for

hydrosilylation reactions. By platinum group it is meant ruthenium, rhodium, palladium, osmium, iridium and platinum and complexes thereof. Platinum group metal-containing catalysts useful in preparing the compositions of the present invention are the platinum complexes prepared as described by Willing, U. S. Pat. No. 3,419,593, and Brown et al, U. S.

5 Pat. No. 5,175,325, each of which is hereby incorporated by reference to show such complexes and their preparation. Other examples of useful platinum group metal-containing catalysts can be found in Lee et al., U. S. Pat. No. 3,989,668; Chang et al., U. S. Pat. No. 5,036,117; Ashby, U. S. Pat. No. 3,159,601; Lamoreaux, U. S. Pat. No. 3,220,972; Chalk et al., U. S. Pat. No. 3,296,291; Modic, U. S. Pat. No. 3,516,946; Karstedt, U. S. Pat. No.

10 3,814,730; and Chandra et al., U. S. Pat. No. 3,928,629 all of which are hereby incorporated by reference to show useful platinum group metal-containing catalysts and methods for their preparation. The platinum-containing catalyst can be platinum metal, platinum metal deposited on a carrier such as silica gel or powdered charcoal, or a compound or complex of a platinum group metal. Preferred platinum-containing catalysts include chloroplatinic acid, 15 either in hexahydrate form or anhydrous form, and or a platinum-containing catalyst which is obtained by a method comprising reacting chloroplatinic acid with an aliphatically unsaturated organosilicon compound such as divinyltetramethyldisiloxane, or alkene-platinum-silyl complexes as described in U.S. Patent Application No. 10/017229, filed December 7, 2001, such as (COD)Pt(SiMeCl₂)₂, where COD is 1,5-cyclooctadiene and Me 20 is methyl. These alkene-platinum-silyl complexes may be prepared, for example by mixing 0.015 mole (COD)PtCl₂ with 0.045 mole COD and 0.0612 moles HMeSiCl₂.

[0052] The appropriate amount of the platinum group metal-containing catalyst will depend upon the particular catalyst used. The platinum catalyst should be present in an amount 25 sufficient to provide at least 2 parts per million (ppm), preferably 5 to 200 ppm of platinum based on total weight percent solids (all non-solvent ingredients) in the composition. It is highly preferred that the platinum is present in an amount sufficient to provide 5 to 150 weight ppm of platinum on the same basis. The catalyst may be added as a single species or as a mixture of two or more different species. Adding the catalyst as a single species is 30 preferred. The platinum group metal-containing catalyst is commercially available or may be made by methods known in the art.

[0053] Component (i) of the present method is prepared by mixing organohydrogensilicon compounds as described above with at least one compound having at least one aliphatic unsaturation as described above in the presence of a platinum group-containing catalyst. The ratio of aliphatic unsaturation to Si-H can be from 100 to 1, preferably from 1.5 to 1. It is most preferred that a sufficient ratio of aliphatic unsaturation to Si-H be added so that all silicon-bonded hydrogen bonds on the organohydrogensilicon compound be reacted. These materials can be mixed together using any suitable mixing means, such as a spatula, a drum roller, a mechanical stirrer, a three roll mill, a sigma blade mixer, a bread dough mixer, and a two roll mill. The temperature of the reaction is not strictly specified, but generally falls within the range of about 20° to 150° C. The length of reaction time is also not critical, and is generally determined by the addition rate of controlling reagent. Optionally, the reaction can be run using common solvents such as toluene, xylene, methylisobutylketone, and heptane.

[0054] Component (ii) of the present method comprises at least one endblocker described by formula (IV) $R'_3SiO(MeR'SiO)_zSiR'_3$ where z ranges from 0 to 150, and R' is independently chosen from alkyl, aryl, alkenyl, dienyl or functional alkyls where the functionality may be fluoro, fluoroether, polyether, ether, aryl, silyl, siloxy, carboxy, glycosidyl or acrylate.

[0055] Examples of alkyl groups of R' include groups having the formula C_nH_{2n+1} , where n is an integer from 1 to 30; cycloaliphatic groups such as cyclohexyl, multivalent alkyl bridges such as derived from trivinylcyclohexane or doubly reacted dienes. Example of alkenyl groups include vinyl and higher alkenyls such as 5-hexenyl, 6-heptenyl, 7-octenyl, 8-nonenyl, 9-decenyl, 10-undecenyl and cyclohexenylethyl. Examples of dienyl substitution include 4,7-octadienyl, 5,8-nonadienyl, 5,9-decadienyl, 6,11-dodecadienyl, and 4,8-nonadienyl. Examples of aryl groups include phenyl, tolyl and xylyl. Examples of functional alkyls include fluoroalkyls such as chloromethyl, trifluoropropyl, and hexafluorobutylethyl; fluoroalkylethers such as $CH_2CH_2CH_2O(CH_2)_2(CF_2)_nCF_3$ where n is an integer from 1 to 10; polyethers such as polyalkyleneglycol monoallyl ethers,

polyalkyleneglycol monovinylether, polyalkyleneglycol allylmethyl ethers, polyalkyleneglycol vinylmethylether, polyalkyleneglycol allyl acetate and polyalkyleneglycol vinylacetate; aralkyls such as benzyl, styryl, and alpha-methylstyryl; alkylsilyls such as methyltrimethylsilane and hexyltrimethylsilane; 5 alkylsiloxanes such as ethylpentamethyldisiloxane or hexylpentamethyldisiloxane; acrylates such as allylmethacrylate; ethers such as vinylphenylether; acetates such as vinylacetate; glycosidyls such as allylglucosides with the general formula of allyl- $C_5H_5(OR)_4$. It is preferred that each R' is independently chosen from alkyl, aryl, fluoroalkyl, fluoroalkylether, alkenyl or polyalkenylglycols. It is more preferred that 10 each R' is independently chosen from alkyl, fluoroalkyl, or alkenyl. Each R' can be identical or different, as desired.

[0056] Subscript z is an integer from 0 to 150. Preferably, z is an integer from 0 to 50. More preferably, z is an integer from 0 to 8.

15 [0057] Component (ii) may be added in amounts from 0.5 to 5000 parts by weight per 100 parts by weight of component (i), preferably 3 to 1000 parts by weight on the same basis and most preferably from 10 to 150 parts by weight on the same basis. Component (ii) may be a single species or a mixture of different species. Component 20 (ii) is commercially available or may be made by methods known in the art.

[0058] Optional component (iii) of the present method comprises at least one organosiloxane chosen from a hydrolyzate described by formula (V) $HO(MeR'SiO)_yH$ or a cyclosiloxane described by formula (VI) $(MeR'SiO)_y$ where y is an integer from 3 to 30, y' is 25 an integer from 1 to 500 and each R' is independently chosen from alkyl, aryl, alkenyl, dienyl or functional alkyls where the functionality may be fluoro, fluoroether, polyether, ether, aryl, silyl, siloxy, carboxy, glycosidyl or acrylate. This component can be added when additional silicone is needed to build molecular weight or increase the degree of polymerization.

30 [0059] Each R' group of formulas (V) and (VI) is independently chosen from alkyl, aryl, alkenyl, dienyl or functional alkyls where the functionality may be fluoro, fluoroether,

polyether, ether, aryl, silyl, siloxy, carboxy, glycosidyl or acrylate. Examples of useful R' groups are as described above.

5 [0060] Subscript y is an integer from 3 to 30, preferably from 3 to 10. Subscript y' is an integer from 1 to 500, preferably from 1 to 200.

10 [0061] Component (iii) may be added in amounts from 0 to 45,000 parts by weight per 100 parts by weight of component (i), preferably 0 to 1000 parts by weight on the same basis, more preferably 100 to 1000 parts by weight on the same basis.
Component (iii) may be a single species or a mixture of different species. It may also comprise materials described solely by formula (V) or formula (VI) or mixtures thereof. Component (iii) is commercially available or may be made by methods known in the art.

15 [0062] Although specific functional groups are described above, generally the only limitation on the functional group is the ability of the particular functional group to withstand the desired equilibration conditions employed. Those knowledgeable in the art can select the appropriate combination of functionality, catalyst and conditions to ensure reaction.

20 [0063] The catalyst used in the present method can be any of a wide variety of catalysts known in the art that are useful in reactions for the ring opening polymerization of cyclosiloxanes. Examples of some appropriate types of catalysts are alkali metal hydroxides, alkali metal alkoxides, alkali metal silanolates, sulfuric acid, hydrochloric acid, Lewis acids such as boron trifluoride and aluminum chloride,
25 tetramethylammonium hydroxide, tetrabutylphosphonium silanolate, quaternary ammonium and phosphonium boron complexes, quaternary ammonium phosphates, quaternary ammonium borates, quaternary ammonium carbonates, quaternary ammonium silicates, trifluoromethane sulfonic acid (triflic acid), phosphonitrile halides (acidic phosphazenes), and phosphazene bases, which are described in U.S.
30 Pat. No. 5,344,906; U.S. Pat. No. 5,670,596; U.S. Pat. No. 5,830,969; and U.S. Pat. No. 5,883,215.

[0064] As a particular example, some suitable alkali metal silanolates and alkali metal siloxanates which can be used are sodium trimethylsilanolate $(\text{CH}_3)_3\text{Si}(\text{ONa})$, sodium triphenylsilanolate $(\text{C}_6\text{H}_5)_3\text{Si}(\text{ONa})$, disodium diphenylsilanolate $(\text{C}_6\text{H}_5)_2\text{Si}(\text{ONa})_2$, disodium dimethylsilanolate $(\text{CH}_3)_2\text{Si}(\text{ONa})_2$,
5 disodium methylaminopropylsilanolate $(\text{CH}_3)[\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2]\text{Si}(\text{ONa})_2$, their potassium equivalents, dipotassium dimethylsilanolate $\text{KO}[(\text{CH}_3)_2\text{SiO}]\text{K}$, dipotassium dimethylsiloxanolate $\text{KO}[(\text{CH}_3)_2\text{SiO}]_n\text{K}$ where n is 4-8, dipotassium phenylmethylsilanolate $\text{KO}[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{SiO}]\text{K}$, and dipotassium phenylmethylsiloxanolate $\text{KO}[(\text{C}_6\text{H}_5)(\text{CH}_3)\text{SiO}]_n\text{K}$ where n is 4-8.

10 [0065] Preferred catalysts are triflic acid, dipotassium dimethylsilanolate, phosphazene bases, acid ion exchanges resins and acid clays.

15 [0066] The amount of active catalyst, excluding any inert supporting material, that is useful ranges from about 10 parts per million (ppm) to 2 parts by weight based on total weight percent solids (all non-solvent ingredients) in the composition. While polymerization can be achieved by using more or less than these amounts, this is not practical, as in the former case excessive amounts of acid would be required for neutralization of the catalyst at the end of the reaction, while in the latter case the use
20 of only trace amounts of catalyst could hinder its effectiveness in the initial reaction.

[0067] The catalyst may be a single species or a mixture of different species. The catalyst is commercially available or may be made by methods known in the art.

25 [0068] Except for the presence of the organohydrogensilicon compounds used to make the reaction product of component (i), the equilibration method employed herein is generally known in the art. U.S. Pat. No. 2,868,766, U.S. Pat. No. 2,994,684, and U.S. Pat. No. 3,002,951 each of which is hereby incorporated by reference, relate to methods of making various types of polymers by polymerizing and
30 copolymerizing cyclic type siloxane species at elevated temperatures, in the presence of a catalyst, for a time sufficient to obtain the desired state of polymerization.

[0069] Thus, for example, polymerization of components (i), (ii), and optionally (iii) can be carried out at a temperature ranging from 30 to 250 °C for a time ranging from 5 minutes to three days. Generally, polymerization can be accelerated by increasing the reaction temperature.

[0070] While it is preferred to carry out the reaction in the absence of a solvent, the reaction can be conducted in the presence of solvents such as acetonitrile, dimethylformamide, decahydronaphthalene, toluene, p-chloro-toluene, o-dichloro-benzene, tetrahydrofuran, xylene, dimethyl sulfoxide, or dibutyl ether, if desired.

[0071] Any of the essential and optional components used in carrying out the polymerization reaction can be combined in stoichiometric quantities necessary to achieve the desired distribution of repeating units in the polymer chain of the polymer composition.

[0072] Another embodiment of the present invention comprises the branched polymers prepared by the method claimed herein. Another embodiment includes compositions comprising the branched polymers prepared by the method claimed herein. A specific preferred composition comprises branched polymers made by the present method, Si-H crosslinker, platinum-group containing catalyst, inhibitor and optionally release modifier and additives for e.g. anchorage. These ingredients, other than the branched polymers made by the present method, are all well known in the art.

[0073] The branched polymers prepared by the present method are particularly useful because they enable the production of low viscosity, high Dp (degree of polymerization), branched polymers. In addition, due to the use of a cyclic branched intermediate without end-groups, it is possible to independently control the properties of branching, end-group level, end-group identity, and Dp. Among other uses, these polymers can be used as fluids, crosslinkers, release polymers, anchorage additives, refractive index modifiers, etc.

EXAMPLES

[0074] Silicon 29 Nuclear Magnetic Spectroscopy (^{29}Si NMR) ^{29}Si NMR data was collected on a Varian Mercury 300 using chloroform D solvent. The experiment was

conducted with a relaxation delay of 60 sec with a gated decoupled pulse sequence using a 5 mm switchable PFG probe was used. Alternatively, the sample was run on a Mercury 400 using a Nalorac 16 mm silicon free Pulsetune® probe with 0.03 M Cr(acac)₃ as a relaxation reagent and gated decoupling to ensure quantitative conditions. Both used 90 degree pulsewidth and the 400 used a 12 sec relaxation delay.

[0075] Si-H Measurement – The material was measured out (according to estimated Si-H content) in 125 mL Erlenmeyer flask to nearest 0.01 grams and sample weight recorded. To this was added 20 mL of prepared mercuric acetate solution (4% mercury acetate powder, 96% (1:1 mixture) methanol/chloroform), the flask was then covered and swirled to mix. A blank sample (no Si-H containing material added) was also prepared for comparison. After samples stood for 30 minutes, they were quenched with 20 mL of prepared calcium chloride solution (25% calcium chloride, 75% methanol). Then 10 drops of prepared phenolphthalein solution (1% phenolphthalein in ethanol) from small pipet was added. The samples were then titrated with 0.1N methanolic potassium hydroxide and measurements taken.

[0076] Vinyl Titration: A sample was weighed to the nearest 0.01 g into a 250 mL iodine flask. Methylene chloride (50.0 mL) was added to dissolve the sample, followed by iodine monochloride (20.0 mL). The sample is placed in the dark for 2 hours. After this period, KI solution (10% KI in DI water; 15.0 mL) is added followed by DI water (50.0 mL). The contents of the flask are swirled to mix well, then the liberated iodine titrated with sodium thiosulfate solution (0.1N in DI water).

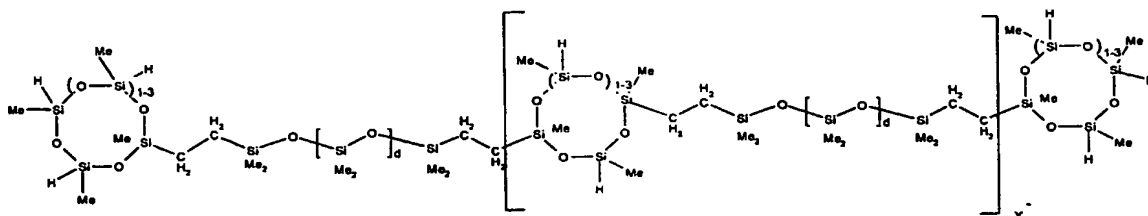
[0077] Gel Permeation Chromatography (GPC) – GPC data was collected using a Waters 515 pump, a Water 717 autosampler and a Waters 2410 differential refractometer. The separation was made with two (300 mm x 7.5 mm) Polymer Laboratories Plgel 5 um Mixed-C columns, preceded by a Plgel 5 um guard column. HPLC grade toluene eluent was used at 1.0 mL/min flowrate and columns and detector were heated to 45° C. An injection volume of 50 uL was used and the sample prefiltered through a 0.45 um PTFE syringe filter. Molecular weight averages were determined relative to a calibration curve(4th order) created using

polydimethylsiloxane (PDMS) standards covering the molecular weight range of 1300 – 850,000.

5 [0078] Measurement of Cure – To measure cure based on percent extractable silicone, a sample of silicone coated substrate was taken in the form of a circular disk. After obtaining an initial coat weight measurement on the sample by X-ray fluorescence (XRF) on an Oxford *Lab-X 3000* Benchtop XRF Analyzer, it was submerged in methylisobutyl ketone (MIBK), with agitation, for 30 minutes. After MIBK extraction, the sample was removed from the MIBK solvent, allowed to air dry and a second coat weight measurement acquired. The
10 percent extractable silicone is defined as the percent loss in silicone coat weight.

Preparation of Organohydrogensilicon Compound

[0079] To a reaction vessel was added 2947 g of a poly(methylhydrogen) cyclic siloxane
15 (MeH cyclics) having an average Dp of about 4.4 (49.1 moles Si-H) (A-1) and 5053 g of a dimethylvinylsiloxyl end-blocked polydimethylsiloxane polymer having an average Dp of about 8 (14.4 moles vinyl) (B-1) to give an Si-H/SiVi ratio of 3.4:1. The polymers were well mixed and a vinylsiloxane diluted platinum (Pt) catalyst added to give a Pt content of about 12 ppm. An exothermic reaction was initiated and over a period of 10 minutes the
20 temperature of the vessel contents rose from 25° C to 137° C. After cooling for 2 hours, bis(2-methoxy-1-methylethyl)maleate (80 g, 1 wt %) was added to stabilize the Pt from further activity. The resulting polymer was not stripped and was shown by GC to have a remaining unreacted MeH cyclics content of about 4 %. The isolated product had a viscosity of 78 mPa.s, a Si-H level of 0.42 wt % (Si-H as H) as determined by titration and a GPC Mn
25 = 2810 and Mw = 8115 vs polydimethylsiloxane (PDMS) standards. ²⁹Si NMR analysis of the product demonstrated that all vinyl functionality has been consumed yielding silethylene bridges, no ring opening has occurred and that the resulting molecular structure is consistent with a methylhydrogen cyclic siloxane capped linear siloxane polymer as described below, where Me is methyl, x is an average of 6.5 for Mw and an average of 1.5 for Mn and d is an
30 average of about 8.



Preparation of Branched Intermediate A

- 5 [0080] A 2 L 3 neck flask was equipped with a condenser, stirrer, thermometer, nitrogen purge and addition funnel. Methyl hydrogen cyclics of avg. Dp = 4.4 (319.2 g, 5.3 mol Si-H) along with vinyl terminated polydimethylsiloxane of avg. Dp = 8 (547.3 g, 1.74 mol Vi) were added to the flask and well mixed. A siloxane complexed Pt catalyst was added to provide a Pt level of 12 ppm. An exothermic reaction was initiated and the temperature of
- 10 the reactants quickly rose to 132 °C over about 10 minutes. After the exotherm had subsided, the mixture was cooled to 45 °C and 1-hexene (331.4 g, 3.9 mol Vi) was added dropwise to keep the exotherm controlled between 35-50 °C. After addition was complete, the reaction mixture was cooled to 25 °C and stripped at 150 °C/1mm Hg to remove volatile material. The reaction product (Intermediate A) was clear, slightly viscous and had an amber tint.
- 15 Based on analysis of the branched polymers produced, synthesis of the desired hexyl capped intermediate was achieved.

Preparation of Branched Intermediate B

- 20 [0081] A 500 mL 3 neck flask was equipped with a stirrer, thermometer, nitrogen purge and addition funnel. Methyl hydrogen cyclics of average Dp = 4.4 (58.9 g, 0.98 mol Si-H) along with vinyl terminated polymer of average Dp = 8 (101.0 g, 0.29 mol Vi) were added to the flask and well mixed. A siloxane complexed Pt catalyst was added to provide a Pt level of 10 ppm. An exothermic reaction initiated and the temperature of the reactants rose to 115 °C over 15 minutes. After cooling, this product was placed in the addition funnel and added
- 25 dropwise to vinylcyclohexene (74.5 g, 0.69 mol terminal vinyl) which had been heated to 86 °C. An exothermic reaction was initiated and was controlled by addition rate to keep the

temperature below 115 °C. After complete addition, the reactant mixture was heated at 115 °C for an additional 2 hours. The reaction product (Intermediate B) was cooled and stripped at 100 °C/ 2 mm Hg to remove volatile species and gave a slightly hazy fluid of 960 cP. Analysis by NMR showed no residual Si-H and gave a spectrum consistent with the desired product.

Examples 1-7: Synthesis of Branched Polymers

[0082] A 2 L 3 neck flask was equipped with a condenser, stirrer, nitrogen purge and thermometer. To the flask was added branched intermediate (Intermediate A or B), the desired endblocker and dimethyl cyclic siloxanes (mixture of D₄ and D₅). The contents were mixed and heated to 40 °C then potassium silanolate catalyst added. The equilibration reaction was conducted at 150 °C overnight, then cooled to 50 °C before addition of acetic acid to neutralize the potassium catalyst. The contents were cooled to 25 °C and stripped at 150 °C/1mm Hg using a wiped film evaporator. The stripped polymer was filtered through a pressure filter. GPC, ²⁹Si NMR and ¹³C NMR data was collected on each branched polymer and supports the polymer structures indicated in Table 1.

Examples 8-9: Synthesis of Branched Polymers

[0083] A 2 L 3 neck flask was equipped with a condenser, stirrer, nitrogen purge and thermometer. To the flask was added Branched Intermediate A, the desired endblocker and dimethyl cyclic siloxanes (mixture of D₄ and D₅). The contents were mixed and heated to 40°C then potassium silanolate catalyst added. The equilibration reaction was conducted at 150 °C overnight, then cooled to 50 °C before addition of acetic acid to neutralize the potassium catalyst. The contents were cooled to 25 °C and stripped at 150 °C/1mm Hg using a wiped film evaporator. The stripped polymer was filtered through a pressure filter. GPC, ²⁹Si NMR and ¹³C NMR data was collected on each branched polymer and supports the polymer structures indicated in Table 2.

Table 1.

| Sample | Branched Intermediate (g) | Endblocker (g) | Dimethyl Cyclics (g) | K + catalyst (g) | Acetic Acid (g) | Dp | Branch units | Endblock Group | % Vi | Viscosity (cP) |
|-----------|---------------------------|--------------------|----------------------|------------------|-----------------|-----|--------------|---|------|----------------|
| Example 1 | A, 174.5 | A, 107.7 | 715.8 | 2.0 | 7.0 | 300 | 6 | SiMe ₂ Vi | 0.84 | 430 |
| Example 2 | A, 60.5 | A, 56.0 | 881.5 | 2.0 | 7.0 | 300 | 2 | SiMe ₂ Vi | 0.47 | 905 |
| Example 3 | A, 311.3 | 192.5 | 494.5 | 2.0 | 7.0 | 160 | 6 | SiMe ₂ Vi | 1.33 | 180 |
| Example 4 | A, 111.4 | 103.1 | 783.5 | 2.0 | 7.0 | 160 | 2 | SiMe ₂ Vi | 0.75 | 288 |
| Example 5 | A, 152.9 | 106.1 | 739.0 | 2.0 | 7.0 | 230 | 4 | SiMe ₂ Vi | 0.76 | 397 |
| Example 6 | A, 179.2 | A, 77.4 B, 47.0 | 721.3 | 2.1 | 7.0 | 300 | 6 | SiMe ₂ Vi SiMe ₃ | 0.56 | 395 |
| Example 7 | A, 174.5 | A, 53.9 B, 76.2 | 693.4 | 2.0 | 7.0 | 300 | 6 | SiMe ₂ Vi SiMe ₃ | 0.41 | 387 |

Endblocker A: vinyltrimethylsiloxy endblocked polydimethylsiloxane fluid of average Dp = 8.

Endblocker B: trimethylsiloxy endblocked polydimethylsiloxane fluid of average Dp = 5.

Table 2

| Sample | Branched Intermediate (g) | Endblocker (g) | Dimethyl Cyclics (g) | K + catalyst (g) | Acetic Acid (g) | Dp | Branch units | Endblock Group | % Vi | Viscosity (cP) |
|-----------|---------------------------|----------------|----------------------|------------------|-----------------|------|--------------|-------------------|------|----------------|
| Example 8 | A, 10.9 | B, 9.6 | 179.2 | 0.5 | 4.0 | 1000 | 6 | SiMe ₃ | --- | Example 8 |
| Example 9 | A, 14.5 | B, 14.2 | 170.9 | 0.4 | 1.0 | 500 | 4 | SiMe ₃ | --- | Example 9 |

Endblocker B: trimethylsiloxy endblocked polydimethylsiloxane fluid of average Dp = 5.

Branched Polymer Coating

[0084] The branched polymers made in Examples 1-7 were mixed with Si-H crosslinker, catalyst, and inhibitor in the amounts described below. Control sample (A) used a vinyl dimethylsiloxo- terminated poly(dimethylsiloxane-silicate) copolymer of 160 Dp and (B) used a linear vinyl dimethylsiloxo-terminated polydimethylsiloxane of Dp = 130; both commercially proven. The coating composition was applied to the specified substrate in sheet form using a pressure blade coater and cured immediately in an oven equipped with a moving web. The cure/release data is summarized in Table 3.

| | | |
|----|---|---------------------|
| 10 | Examples 1-7 Polymer | 10.00 g |
| | Crosslinker (Si-H homopolymer of Dp ~ 20) | 0.33 g |
| | Bis(2-methoxy-1-methylethylmaleate) inhibitor | 0.04 g |
| | Pt in siloxane | 0.19 g |
| | Cure temp./time | 149°C(300°F)/ 6 sec |
| 15 | Si-H/SiVi ratio | 1.6 |
| | Substrate | SCK paper |

Table 3.

| Example | Structure Dp/ branches/endgroups* | Extractable silicone(%) | Release Force(g/in) @ 12 in/min; TESA® 7475 adhesive* | Release Force (g/in) @ 4000 in/min, TESA® 7475 adhesive* |
|-----------|---|--------------------------------|---|--|
| Example 1 | 300/6/8 MVi | 4.8 | 15 | 44 |
| Example 2 | 300/2/4 MVi | 4.4 | 14 | 58 |
| Example 3 | 160/6/8 MVi | 3.5 | 20 | 50 |
| Example 4 | 160/2/4 MVi | 4.8 | 52 | 86 |
| Example 5 | 230/4/6 MVi | 4.2 | 27 | 56 |
| Example 6 | 300/6/5.6 MVi, 2.4 M | 11.1 | ----- | ----- |
| Example 7 | 300/6/4 MVi, 4 M | 18.9 | ----- | ----- |
| Control A | 160/1/4 MVi | 2.2 | 29 | 52 |
| Control B | 130/0/2 MVi | 5.5 | 25 | 74 |

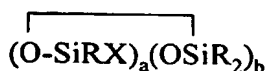
• M = Me₃SiO

• MVi = ViMe₂SiO

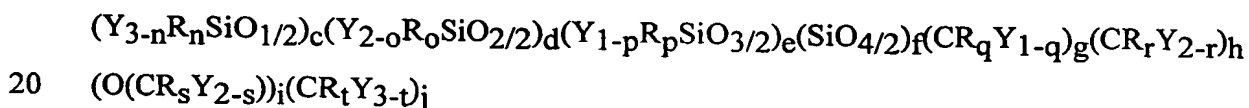
TESA® 7475 Adhesive is a solvent acrylic adhesive available in a tape format.

CLAIMS

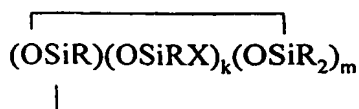
1. A method comprising heating in the presence of a catalyst, a mixture comprising
 (i) a reaction product obtained by mixing in the presence of a platinum group metal-
 5 containing catalyst at least one organohydrogensilicon compound containing at least one
 silicon-bonded hydrogen atom per molecule and at least one compound having at least one
 aliphatic unsaturation; where the organohydrogensilicon compound is described by formula
 (I)



- 10 where each R is independently selected from a hydrogen atom and a monovalent hydrocarbon
 group comprising 1 to 20 carbon atoms which is free from aliphatic unsaturation, a is an
 integer from 1 to 18, b is an integer from 1 to 19, a + b is an integer from 3 to 20, each X is
 an independently selected functional group selected from a halogen atom, an ether group, an
 alkoxy group, an alkoxyether group, an acyl group, or a silyl group, or a -Z-R⁴ group, where
 15 each Z is independently selected from an oxygen and a divalent hydrocarbon group
 comprising 2 to 20 carbon atoms, each R⁴ group is independently selected from -BR_uY_{2-u}, -
 SiR_vY_{3-v}, or a group described by formula (II):



- where B refers to boron, each R is as described above, the sum of c+d+e+f+g+h+i+j is at
 least 2, n is an integer from 0 to 3, o is an integer from 0 to 2, p is an integer from 0 to 1, q is
 an integer from 0 to 1, r is an integer from 0 to 2, s is an integer from 0 to 2, t is an integer
 25 from 0 to 3, u is an integer from 0 to 2, v is an integer from 0 to 3, each Y is an independently
 selected functional group selected from a halogen atom, an ether group, an alkoxy group, an
 alkoxyether group, an acyl group, or a silyl group, or a Z-G group, where Z is as described
 above, each G is a cyclosiloxane described by formula (III):



where R and X are as described above, k is an integer from 0 to 18, m is an integer from 0 to 18, k+m is an integer from 2 to 20, provided in formula (II) that one of the Y groups is replaced by the Z group bonding the R⁴ group to the cyclosiloxane of formula (I), and

5 provided further at least one X group of Formula (I) is a -Z-R⁴ group;

(ii) at least one endblocker described by formula (IV) R'₃SiO(MeR'SiO)_zSiR'₃,

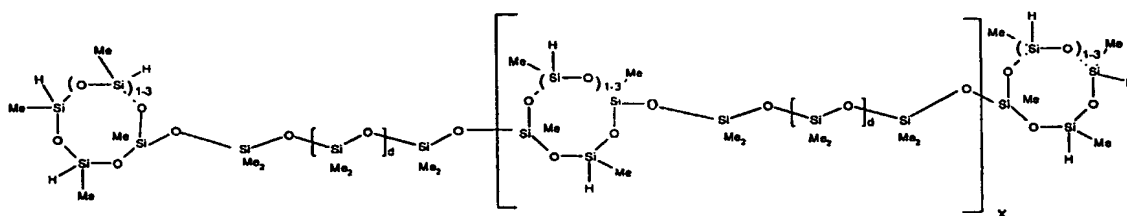
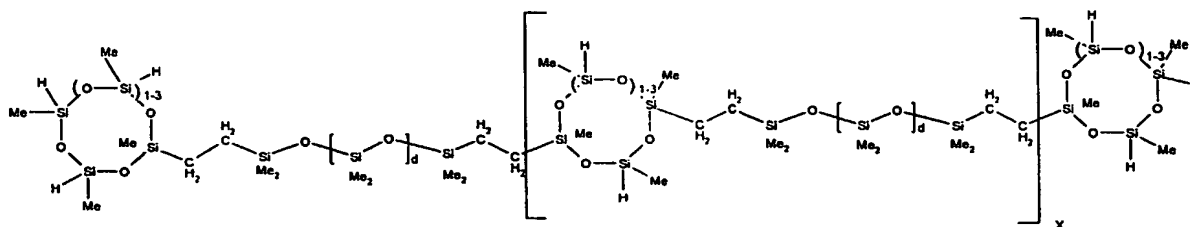
where z ranges from 0 to 150 and each R' is independently chosen from alkyl, aryl, alkenyl, dienyl or functional alkyls where the functionality may be fluoro, fluoroether, polyether, ether, aryl, silyl, siloxy, carboxy, glycosidyl or acrylate, and optionally

10 (iii) at least one organosiloxane chosen from a hydrolyzate described by formula (V) HO(MeR'SiO)_yH and a cyclosiloxane described by formula (VI) (MeR'SiO)_y where y is an integer from 3 to 30, y' is an integer from 1 to 500, and each R' is as described above; so to cause polymerization of components (i), (ii), and optionally (iii) to form branched polymers.

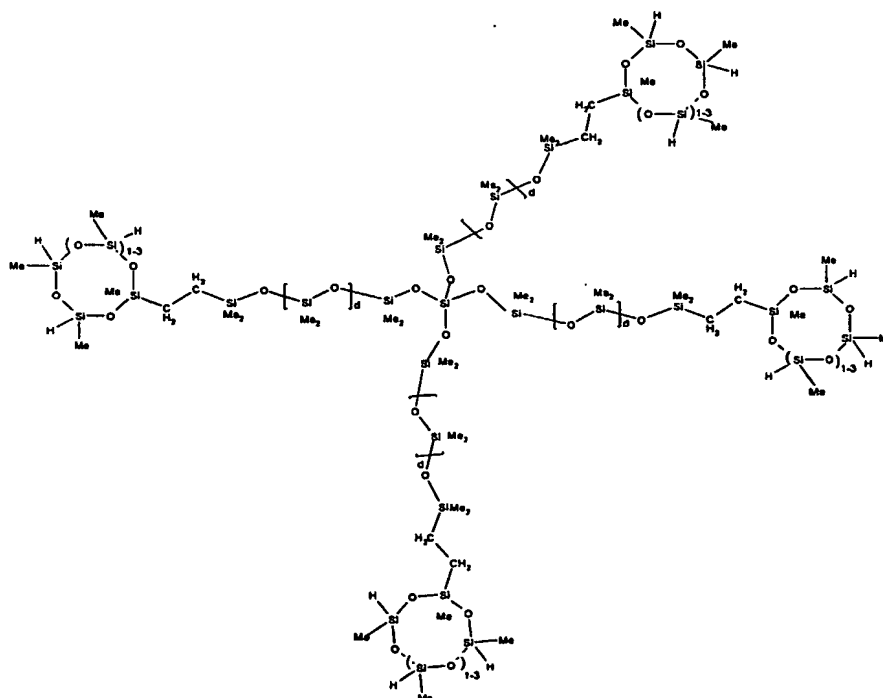
15 2. The method of claim 1 where subscript b is an integer from 2 to 19, subscript c is an integer from 0 to 50, subscript d is an integer from 0 to 5000, subscript e is an integer from 0 to 48, subscript f is an integer from 0 to 24, subscript g is an integer from 0 to 50, subscript h is an integer from 0 to 50, subscript i is an integer from 0 to 50, and subscript j is an integer from 0 to 50.

20 3. The method of claim 1 or 2 where each R group is independently selected from hydrogen atoms, alkyl groups comprising 1 to 8 carbon atoms, or aryl groups comprising 6 to 9 carbon atoms, each X is a Z-R⁴ group or is independently selected from chloro, methoxy, isopropoxy, where Z is a divalent hydrocarbon group, and R⁴ is selected from -CH₂CH₂-, -CH₂CH₂CH₂CH₂-, -O(CH₂CH₂O)_{z'}-, where z' = 1-100, O(CH₂CH₂CH₂O)_{z''}-, where z'' = 1-100 and siloxane groups described by -R₂SiO(R₂SiO)_dSiR₂-Z-G, -R₂SiOSiR₃, -R₂SiOSiR₂-Y, and -RSi(OSiR₃)₂, where d is an integer from 1 to 50 and Z, G, and R are as described above.

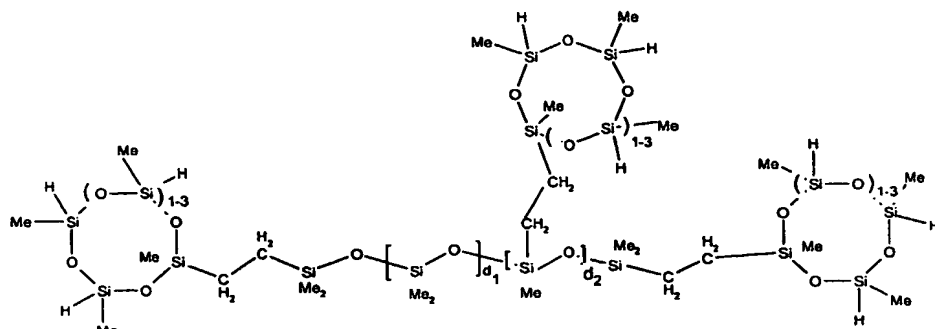
4. The method of any of claims 1 to 3 where the organohydrogensilicon compound is selected from the structures below where Me is methyl, $d^1 + d^2 = d$, and x can range from 1 to 100:



5

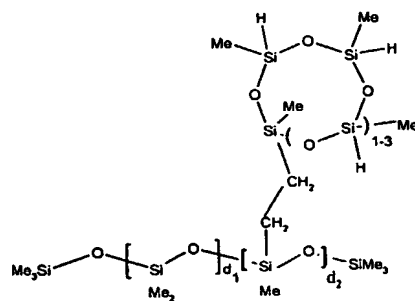
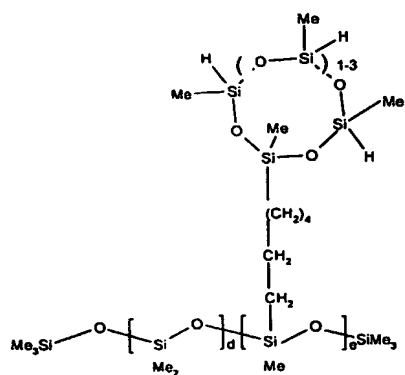


5

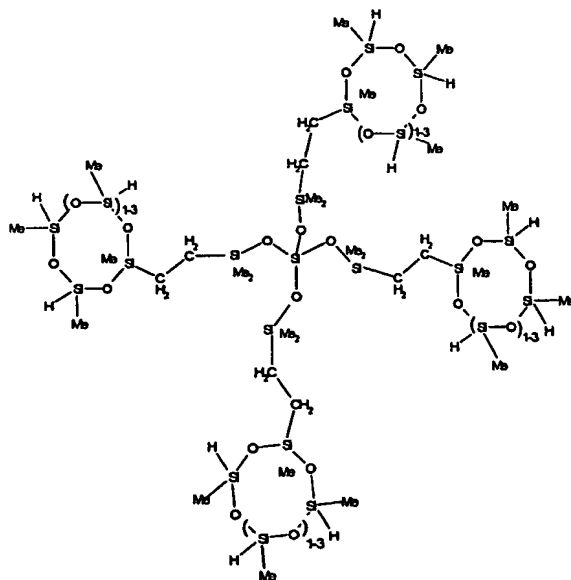


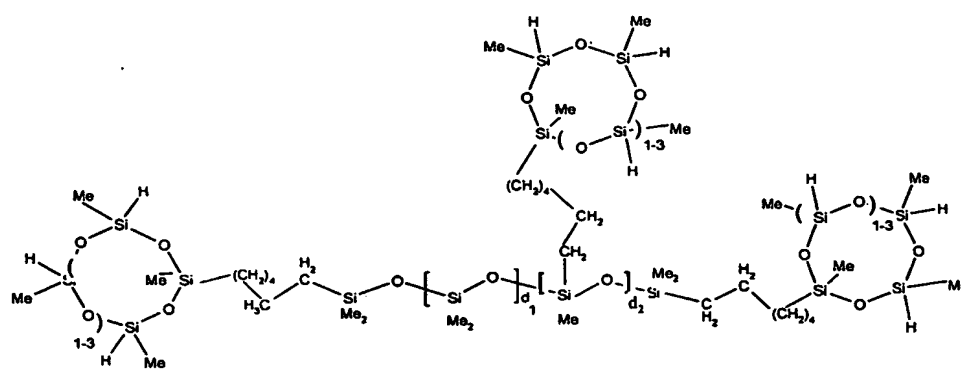
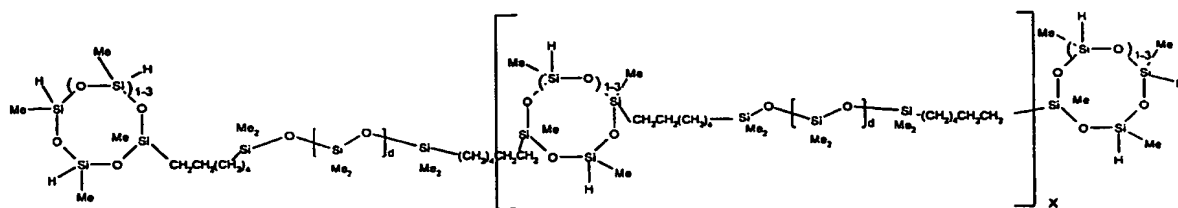
10

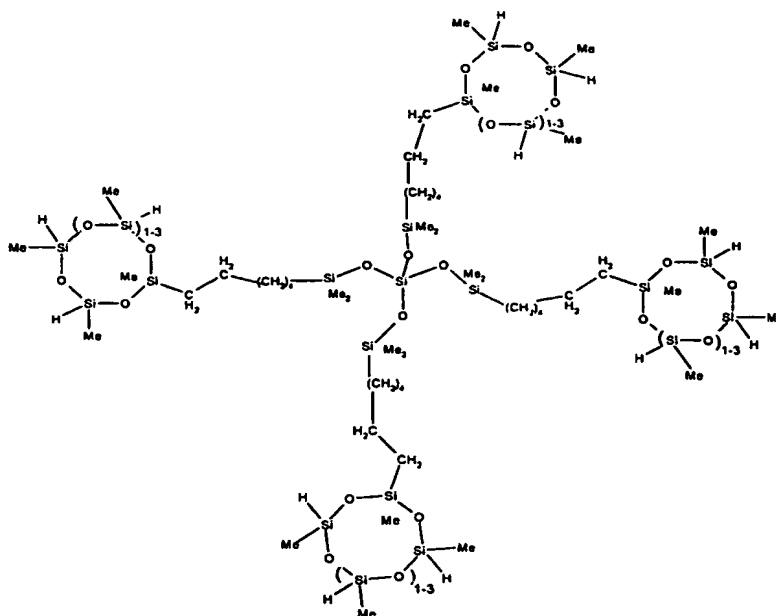
15



20

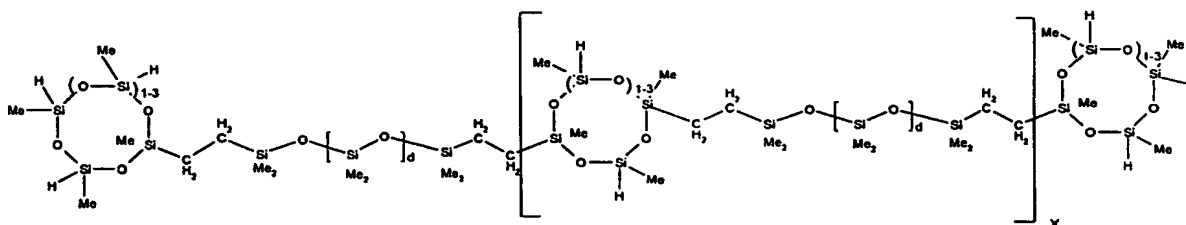






5. The method of any of claims 1 to 4 where the organohydrogensilicon compound is described by the structure below where Me is methyl, d is an average of 8, and x is an integer from 1 to 15.

5



6. The method of any of claims 1 to 5 where R' is independently chosen from alkyl, fluoroalkyl, or alkenyl, component (ii) is added in amounts from 3 to 1000 parts by weight based on 100 parts by weight of component (i), and component (iii) is added in amounts from 0 to 1000 parts by weight.

10

7. The method of any of claims 1 to 6 where R' is independently chosen from alkyl, fluoroalkyl, or alkenyl, component (ii) is added in amounts from 3 to 1000 parts by weight based on 100 parts by weight of component (i), and component (iii) is added in amounts from 0 to 1000 parts by weight.

15

8. The method of any of claims 1 to 7 where a sufficient ratio of aliphatic unsaturation to Si-H is used so that all the silicon-bonded hydrogen bonds on the organosilicon compound are reacted.

5

9. A branched polymer made by the method of any of claims 1 to 8.

10. A composition comprising a branched polymer made by the method of any of claims 1 to 8.

10

11. A composition comprising a branched polymer made by the method of claim 8, a Si-H crosslinker, a platinum-group containing catalyst, and an inhibitor.

10/538682

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 July 2004 (15.07.2004)

PCT

(10) International Publication Number
WO 2004/058857 A3

(51) International Patent Classification⁷: **C08G 77/06**,
77/10, 77/44, 77/442, 77/50, C08F 283/12

SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number:
PCT/US2003/040277

(84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date:
17 December 2003 (17.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/435,824 20 December 2002 (20.12.2002) US

(71) Applicant (*for all designated States except US*): **DOW CORNING CORPORATION** [US/US]; 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **CHAPMAN, Brian**, Douglas [US/US]; 401 Lingle Lane, Midland, MI 48640 (US). **DURFEE, Loren, Dean** [US/US]; 1807 Burlington Drive, Midland, MI 48642 (US). **MITCHELL, Timothy**, Paul [US/US]; 508 Clarion Street, Clio, MI 48420 (US). **VAN DORT, Paul, Cornelius** [US/US]; 3051 North Lakeview Drive, Sanford, MI 48657 (US). **TONGE, James** [US/US]; 3105 North Lakeview Drive, Sanford, MI 48657 (US).

(74) Common Representative: **SCADUTO, Patricia, M.**; IP Department - MS CO 1232, Dow Corning Corporation, 2200 West Salzburg Road, P.O. Box 994, Midland, MI 48686-0994 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
- *of inventorship (Rule 4.17(iv)) for US only*

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) Date of publication of the international search report:
23 September 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BRANCHED POLYMERS FROM ORGANOHYDROGENSILICON COMPOUNDS

(57) Abstract: A method comprising heating in the presence of a catalyst, a mixture comprising (i) a reaction product obtained by mixing in the presence of a platinum group metal-containing catalyst at least one organohydrogensilicon compound containing at least one silicon-bonded hydrogen atom per molecule and at least one compound having at least one aliphatic unsaturation; (ii) at least one endblocker, and optionally (iii) at least one organosiloxane chosen from a hydrolyzate or a cyclosiloxane, so to cause polymerization of components (i), (ii), and optionally (iii) to form branched polymers.

WO 2004/058857 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/40277

| | | |
|--|---|--|
| A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G77/06 C08G77/10 C08G77/44 C08G77/442 C08G77/50 C08F283/12 | | |
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08G C08F C09D | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A,P | WO 03/093369 A (DOW CORNING) 13 November 2003 (2003-11-13) claim 1 | 1 |
| A | US 4 900 779 A (LEIBFRIED) 13 February 1990 (1990-02-13) claim 1 | 1 |
| A | US 5 436 308 A (DURFEE ET AL) 25 July 1995 (1995-07-25) column 3, line 49 - line 59 column 4, line 5 - line 10 | 1 |
| A | US 6 303 729 B1 (SATO) 16 October 2001 (2001-10-16) claim 1 | 1 |
| <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. | | |
| * Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*G* document member of the same patent family</p> </div> </div> | | |
| Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">27 July 2004</div> | | Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">04/08/2004</div> |
| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016 | | Authorized officer <div style="text-align: center; font-weight: bold;">Lentz, J.C.</div> |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/40277

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|----|---------------------|----------------------------|---------------------|
| WO 03093369 | A | 13-11-2003 | WO 03093369 A1 | 13-11-2003 |
| US 4900779 | A | 13-02-1990 | AU 593676 B2 | 15-02-1990 |
| | | | AU 7746187 A | 03-03-1988 |
| | | | BR 8704416 A | 19-04-1988 |
| | | | CA 1295773 C | 11-02-1992 |
| | | | DE 3789475 D1 | 05-05-1994 |
| | | | DE 3789475 T2 | 14-07-1994 |
| | | | EP 0259711 A2 | 16-03-1988 |
| | | | ES 2060588 T3 | 01-12-1994 |
| | | | HK 110394 A | 21-10-1994 |
| | | | KR 134785 B1 | 20-04-1998 |
| | | | MX 7905 A ,B | 01-10-1993 |
| | | | US 5013809 A | 07-05-1991 |
| | | | US 5124375 A | 23-06-1992 |
| | | | US 5124423 A | 23-06-1992 |
| | | | JP 2540726 B2 | 09-10-1996 |
| | | | JP 7003029 A | 06-01-1995 |
| | | | JP 2582524 B2 | 19-02-1997 |
| | | | JP 7003030 A | 06-01-1995 |
| | | | JP 1126336 A | 18-05-1989 |
| | | | JP 1925705 C | 25-04-1995 |
| | | | JP 6055818 B | 27-07-1994 |
| | | | US 4902731 A | 20-02-1990 |
| US 5436308 | A | 25-07-1995 | NONE | |
| US 6303729 | B1 | 16-10-2001 | JP 2000327782 A | 28-11-2000 |